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Molecules as building blocks for a CFD-PBE model to describe the effect of fluid dynamics on nanoparticle formation

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Introduction and motivation

Recently research efforts have focused on the effect of fluid dynamics on particle formation processes, by using special mixing devices, that allow to perform controlled experiments, and complex models, that allow to quantify its influence on the final particle size [1]. The standard modelling approach consists in considering three different steps: nucleation, molecular growth and aggregation. This is usually done by simulating the process with a population balance equation (PBE) coupled with computational fluid dynamics (CFD), in which these three different steps are considered separately. The PBE is often written using as internal coordinate the actual particle size or volume [2]; here, we propose a new modelling strategy that overcomes the concepts of nucleation and molecular growth, by using as internal coordinate the number of molecules which aggregate, or self-assemble, together forming a nanoparticle. The novel modelling approach is therefore defined as a purely-aggregative model.

Theory and model formulation

The main problem with the classical approach lies in the somewhat arbitrary definition of the different steps and in the difficulty related to the derivation of the corresponding rates. The objective of this work is to present and validate a model, developed on molecular building blocks, to describe the effect of fluid dynamics on particle formation processes, overcoming the concept of nucleation and growth by considering molecules as objects aggregating, or self-assembling, between themselves, once the local solubility limit is reached and overcome. This is justified by the fact that particle formation is a supersaturation driven process. As test case, nanoparticle formation via solvent displacement (with acetone and water in the role of solvent and anti-solvent) is considered, by using a polymer (poly- ϵ -caprolactone, PCL) as solute, in a confined impinging jets mixer (CIJM) [1,2]. The choice of a polymer as solute is motivated by the fact that the formed nanoparticles are amorphous, simplifying for this first study the complexity of the problem and leaving the investigation of crystalline systems for future steps. This precipitation process, induced by solvent displacement, is also known as flash nano-precipitation (FNP).

Thanks to supersaturation (due to mixing solvent and anti-solvent), the solute molecules aggregate together forming a new colloidal phase [3]. The model calculates the supersaturation, as the ratio between the local solute concentration and the equilibrium concentration, and when it is greater than one allows the aggregation of two solute molecules, forming a dimer. When the dimer collides with another solute molecule a trimer is formed, and so on for larger clusters: when a cluster of n molecules collides with a cluster of n' molecules, they form a cluster of $n+n'$ molecules (or molecular building blocks, as shown in Fig. 1). For the moment no energy

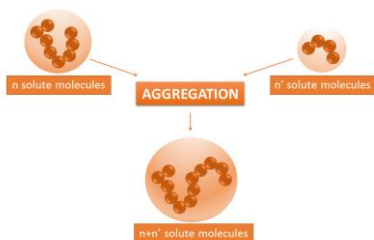


Figure 1. Two nanoparticles, formed by n and n' solute molecules respectively, collide leading to $n+n'$ molecules.

barrier is considered, assuming therefore an unitary aggregation efficiency, as in spinodal decomposition, however its introduction is of course possible. The rate with which solute molecules aggregate is expressed by the aggregation kernel, written in terms of the number of molecules which form a particle (say n), referred to as aggregation number, and considered here as the internal coordinate of the PBE. The aggregation kernel

considers both the aggregation due to molecular diffusion and turbulent fluctuations. The PBE operates therefore on the cluster mass distribution, $f(n)$, quantifying the number of solute molecules belonging to one single nanoparticle.

Operating conditions and numerical details

Model predictions are compared with experiments in terms of the final mean nanoparticle size at the CIJM exit, measured with Dynamic Light Scattering (DLS), and extracted from our simulations by means of the Flory's law, assuming the freely jointed chain hypothesis [4]. In order to save computational cost we solve the PBE in terms of the moments, $m^{(i)}$, of the cluster mass distribution by means of the quadrature methods of moments (QMOM). Moments of different order have different physical meanings: for example the average number of solute molecules per cluster/nanoparticle is expressed as $m^{(1)}/m^{(0)}$. More details on the model are reported in Lavino et al [5]. Another advantage of this modelling approach is that the link to the molecular scale is more evident and easier to establish. For example in our work, the radius of gyration of the solute molecule (and of the cluster/nanoparticle), that appears in the aggregation kernel, is determined through molecular dynamics simulations (full-atom or coarse-grained). All the properties are averaged by means of the Favre-average, in order to take into consideration turbulent and density fluctuations.

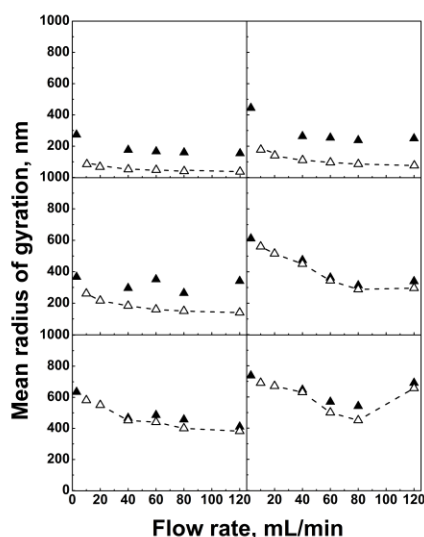


Figure 2. Model predictions (empty symbols) against experimental data (black triangles). From top to bottom and left to right the initial PCL concentration corresponds to 0.5, 2.5, 5.0, 10.0, 15.0, and 25.0 mg/mL

Results and discussion

An example of comparison between simulations and experiments is reported in Fig. 2, where the mean nanoparticle size at the CIJM outlet is reported versus the inlet flow rates of the water and acetone streams at different initial solute concentrations in the acetone solution. As it can be seen, at very low initial solute concentrations a mismatch between experiments and simulations is present, however, starting from medium solute concentrations (5 mg/mL) the agreement with experiments is very good. Looking at Fig. 2, the effect of fluid dynamics is clear: increasing the input flow rate the turbulence of the system increases, decreasing the mixing time and affecting therefore the overall supersaturation, leading to smaller nanoparticles. On the other hand, turbulence also promotes nanoparticle aggregation. These two phenomena have opposite effects and at very high initial solute concentration the latter dominates on the first one, as shown by the minimum in the right-bottom diagram.

In conclusion, the model shows a good agreement with experiments, although future work is recommended in order to understand what kind of phenomena plays a key role at low concentration. We believe moreover that this approach can be extended to a wide spectrum of crystallization and precipitation processes, introducing the role of crystallinity. Moreover, as very often polymers are used as additives to functionalize crystals and particles in general, some of the results obtained in this context

can be directly exploited.

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